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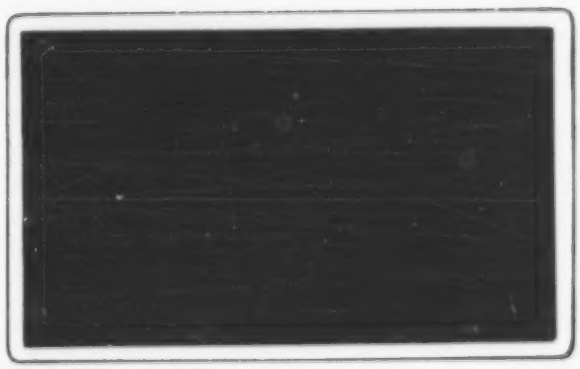

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THE ATMOSPHERIC TRANSPORT OF INSECTICIDES: A LITERATURE REVIEW

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THE ATMOSPHERIC TRANSPORT OF INSECTICIDES: A LITERATURE REVIEW

INTRODUCTION

The atmosphere is probably the most important medium for long distance dispersion of pesticides. Drift and evaporation during ground and aerial application, volatilization from crops and soils, wind erosion of contaminated soil and emissions from manufacturing and disposal processes constantly add to atmospheric burden of pesticides. Prevailing air currents may transport these pesticides and their degradation products great distances. In this manner, pesticides used in one country may reach another in which they have never been used, or are banned. The potential exists even for the introduction of harmful pesticides to the delicate ecosystems of remote regions previously untouched by man, via long-range dispersion in the troposphere. Pesticide residues may be returned from the atmosphere to the surface of the earth by way of rainout, fallout, or direct sorption.

There is a large body of evidence which indicates that pesticides can be translocated great distances from the point of application. The greatest area of concern lies with the high-molecular weight organochlorine insecticides such as DDT, lindane, chlordane, dieldrin and toxaphene. These compounds have been shown to become dispersed throughout the atmosphere on a global scale. Furthermore, those compounds which have the capacity to bioaccumulate present an added risk.

PRODUCTION AND USE OF INSECTICIDES

The most documented organochlorine insecticide is DDT (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane). DDT was introduced in 1943 during World War II to combat tropical typhus and malaria carried by mosquitoes and lice. Peak use and production occurred in the United States and other countries in the late 1950's and early 1960's, reaching its maximum in 1964. At that time an estimated 400,000 tonnes were used annually in agriculture, forestry, public health and other pest control programs. Since 1964, global production has decreased progressively. Use in North America was restricted in 1969 and banned in the United States, Canada and most European countries in 1972. Methoxychlor, the pp'-methoxy analog of DDT is currently not restricted in North America (Stevens and Neilson, 1989).

Because of its effectiveness and relatively low cost, DDT is still used heavily in many areas of the world, particularly the Middle and Far East, Africa and Latin America (Brooks, 1974). In

developing countries, especially in the Southern Hemisphere and tropical regions, the use of chlorinated pesticides such as DDT and HCH is considered inevitable and is expected to increase.

The DDT formulation used for agriculture and malaria control consists roughly of 70% to 80% pp'-DDT and 15% to 20% op'-DDT. It is commonly reported as occurring in the environment as its primary oxidized metabolite, DDE, or the reduced metabolites of DDD and TDE. The collective total will be referred to as total DDT.

HCH (1,2,3,4,5,6-hexachlorocyclohexane) is also an organochlorine insecticide with a history of heavy use throughout the world. It has been applied either as "lindane" which consists of 99% gamma-isomer, or technical HCH. Technical HCH is also referred to as benzene-hexachloride (BHC), and consists of approximately 70% alpha-HCH, 13% gamma-HCH, 7% beta-HCH and 5% delta-HCH. Lindane has generally replaced technical HCH over the past few years as the predominant type used (Brooks, 1974). Like DDT, HCH consumption has been on the decline since the 1970's in North America, and use of technical HCH has been heavily restricted. Today, purified lindane is used in most countries.

Use of the cyclodiene pesticides, aldrin, dieldrin, endrin, heptachlor and heptachlor epoxide has similarly declined in North America. Aldrin and its toxic metabolite dieldrin have been banned in Canada and the United States since the early 1970's. Endrin is currently under restricted use, and heptachlor is banned for agricultural use, although still used commercially. Endosulfan is still used both in Canada and the United States (Stevens and Neilson, 1989). Chlordane is a heavily used insecticide, made of a mixture of some 45 components. The major components are heptachlor, cis- and trans-chlordane, trans-nonachlor and several isomers of chlordene (Jansson, et al. 1979).

Chlorinated terpenes, and specifically toxaphene, have been applied as insecticides for almost thirty years and are presently used in the United States in the southern corn-growing states. For several years this insecticide ranked first in quantity used in the United States. Toxaphene is a mixture of isomers of chlorinated camphenes, containing 67 to 69% chlorine. Although toxaphene has been used as an insecticide for more than 25 years, its chemical structure and composition is relatively unknown. It is a mixture of more than 170 compounds, making environmental identification and quantification extremely difficult (Jansson, et al. 1979).

HISTORICAL PERSPECTIVE

The global distribution of pesticides has been the subject of many investigations over the past three decades. Much of the widespread interest in atmospheric transport of insecticides had its beginnings in a few important findings from the early 1960's. It became apparent that atmospheric transport of these man-made chemicals was possible and the potential existed for global dispersion.

The first indication that these non-volatile organochlorine insecticides were contaminating the atmosphere was discovered in 1964 by Wheatley and Hardman (1965). Monthly rain samples collected in an agricultural area of central England, revealed the presence of the DDT, HCH and dieldrin in parts per trillion levels. Concentrations of the solutes in rainwater samples varied from month to month and appeared to be independent of the total monthly rainfall.

Shortly after, Abbott et al. (1965) confirmed these results, finding comparable levels of DDT, HCH and dieldrin in metropolitan London rain, along with traces of the principle metabolites of DDT, DDE and TDE. Abbott et al. (1966) attempted to further examine atmospheric contamination by examining air samples from London. Although traces of HCH, dieldrin and DDT, DDE and TDE were confirmed, levels were at the limits of sensitivity for detection.

A more comprehensive analysis of rain in the British Isles was conducted by Tarrant and Tatton, (1968) who examined total precipitation in three month periods, during 1967, at several widely distributed sites, including urban, rural, agricultural and remote mountain regions. All sites throughout the year had HCH isomers, dieldrin, DDT, DDE and TDE at lower levels than the earlier studies. A decrease in dieldrin content was speculated to be a result of the abandonment of large scale use of aldrin and dieldrin. Heptachlor epoxide and beta-HCH were also detected in small amounts in some samples.

The global extent of atmospheric contamination by insecticides was questioned by Sladen and Reichel (1966), who, in 1964, found traces of DDT and DDE in the liver and fat of penguins and a seal in the Antarctic. The authors concluded that deep ocean currents, the food chain and animal migrations were the principal mode of contamination. Transport by air was considered unlikely.

Tatton and Ruzicka (1967) examined penguins and their eggs, as well as fish and local birds found on Signy Island in the Antarctic, an area previously untouched by man. Similar levels of DDT, DDE and TDE were found in all species, along with HCH isomers, heptachlor epoxide and dieldrin. The most predominant insecticide was DDE in all species. The authors concluded long

range transport of these insecticides was by sea and air. Their report compared Antarctic results with residues found in the eggs of razorbills, puffins and guillemot collected around the British Isles. These species are considered to be the ecological equivalent to the squa and shags of the Antarctic. Pesticide levels were approximately 50 times higher in the species from the British Isles, indicating that the waters of Antarctica were still far less contaminated than those in the Northern Hemisphere.

The mode of transport of insecticides to the remote Antarctic was examined indirectly in 1966 by analysis of snow melt (Peterle, 1969). Trace, but non-quantifiable, amounts of DDT were confirmed in three of five samples, indicating that contamination by the atmosphere was possible.

The preceeding evidence indicates that insecticides have contaminated extensive areas of the world not directly treated with pesticides. However, the mode of translocation was not clearly understood and could be attributed to food-chain dispersion and water or atmospheric translocation. The relative importance of each mode was unknown.

The first direct evidence of the significance of long distance atmospheric transport of insecticides was presented by Cohen and Pinkerton (1966) in 1965 from analysis of a deposit of dust in the Cincinnati, Ohio area. Results indicated the presence of DDT, DDE, chlordane, heptachlor epoxide and dieldrin in levels of parts per million in the dust samples. This suggests that airborne translocation of contaminated dust could be an important mode of pesticide transport.

The presence of insecticides in remote locations and the discovery of the significance of atmospheric transport during the early 1960s resulted in a large-scale survey to determine the extent of contamination on a global scale. Topics of research include finding indirect and direct evidence of global dispersion, and attempting to answer questions regarding transport mechanisms, the physical state, temporal and spatial variation, and mechanisms of removal and deposition of these chemicals from the atmosphere. These studies are summarized on the following pages.

ATMOSPHERIC TRANSPORT - BIOINDICATORS AS EVIDENCE

The early reports of contamination of seals, penguins, fish and birds in the Antarctica (Sladen and Reichel, 1966; Tatton and Ruzicka, 1967) were generally received with surprise and concern. High molecular weight insecticides, such as DDT and dieldrin, were generally considered non-volatile and their previously unsuspected translocation from areas of application led to widespread interest in determining the true extent of global contamination. Evidence from extensive surveys suggested

indirectly that the atmosphere could possibly be playing a large role in the translocation of insecticide residues since in many cases, especially in the remote Antarctic and Arctic, these insecticides had never been used.

Surveys of insecticide contamination in body tissues of several species of mammals, birds, fish and plants have been conducted in continental regions of North America, Europe, and Iceland, and in open-ocean ecosystems of the Arctic and the Antarctic. Results of these studies are summarized in Table 1. Measurable quantities of DDT and HCH isomers, dieldrin, aldrin, heptachlor epoxide, chlordane and toxaphene have been frequently identified, occasionally at extremely high concentrations. Although the species diversity and widespread locations cause difficulty when comparing residue levels, it appears that DDT residues have been declining since the early 1970's as the parent DDT was not detected in samples collected during the 1980's. This may be a reflection of decline in use since the North American and European ban in 1972. The primary metabolite, p-p'-DDE, is the predominant residue of the DDT group found in most species sampled. Table 1 shows that there was a general increase in HCH isomers. Alpha-HCH became the highest contaminant in biological species rather than DDT residues, which were predominant during the 1960's and early 1970's. Although toxaphene is currently one of the most heavily used insecticides, only three papers reported on contamination levels of this residue. Exceedingly high levels of toxaphene were found in these three cases.

Dybern (1972) demonstrated in 1965-1968 that DDT had accumulated in considerable quantity in animals from the Baltic Sea. Analysis of fat tissue from several species of fish, seal and fish-eating birds indicated high levels of pp'-DDT, especially in white-tailed eagles, where levels ranged from 1 to 250,000 ppm. These levels illustrate the bioaccumulation potential of the DDT group. The presence of residues in the open-ocean ecosystem suggests that considerable quantities of these pesticides have been brought by air and passed through the food chain.

A similar study in the Baltic and North Sea region and at Lake Veneer in Sweden (Jansson, et al. 1979) was conducted from 1974 to 1978. The mean levels of total DDT residues in fish from the Baltic Sea ranged from 6.8 ppm to 8.0 ppm, slightly lower than the earlier study which ranged from 6-31 ppm. Results were 6.8 ppm DDT in Baltic Herring in the second study, compared with 17 ppm in the same species taken in the 1966-68 study. This apparent trend of decreasing DDT residues was not observed in fat tissue from seals captured in the Baltic. The earlier study shows mean residues ranging from 96-170 ppm, compared to a much higher maximum concentration of 970 ppm in the later study. This may be due to the potential for DDT bioaccumulation, whereby decreasing levels of DDT may be less apparent in these species at the top of the food-chain. Residue levels in fish caught in the

widely separated locations of the Baltic, the North Sea and interior Sweden (Lake Vattern) showed similar concentrations, suggesting widespread contamination from a highly dispersed source from the atmosphere, rather than from local point sources. The presence of chlorinated terpenes (toxaphene) and of chlordane residues also strongly suggests the importance of long-range atmospheric transport, since neither chlordane nor toxaphene had ever been used in Sweden.

Hermit crabs taken from the North Sea in a study conducted in 1986 (Knickmeyer and Steinhart, 1988) showed the presence of low levels of DDE and HCH isomers. Slight or no distribution gradients were observed for residue levels in crabs from several widespread locations, indicating that a local source was less likely than long-range transport of these pesticides.

Adipose tissues from mammals in the Greenland Arctic were sampled in 1972 (Clausen, et al. 1974). Low levels of DDE were found in all specimens. Lindane and aldrin were found in most specimens. Traces of heptachlor epoxide were also observed. Polar bears, at the top of this food chain, had the highest levels of all residues except lindane, which is known to have a lower bioaccumulation potential than the DDT group.

Analysis of two species of fish (whole fish basis) for 19 organochlorine contaminants from the remote Hudson Bay lowland in the Canadian Arctic was conducted in 1981 (McCrea and Fischer, 1986). Only trace amounts of alpha-HCH and DDE were occasionally found, at ppb levels, with the parent compound undetected.

From 1980 to 1984, fish species from five lakes in the remote Southern Labrador area of the Canadian sub-arctic were surveyed for organochlorine insecticide contamination (Lockerbie and Clair, 1988). Although the recorded uses of DDT occurred from 1957 to 1961, some 420 km southwest of the region, traces of DDE and DDD were found, along with the alpha and gamma isomers of HCH. This is indicative of long range transport of these compounds in quantities similar to other Arctic results. The parent DDT was undetected. Although levels of insecticide residues were found to be low for species examined in these Arctic studies, the presence of these residues, rather than the absolute quantity, is evidence for atmospheric transport to these remote locations.

The use of mosses and lichens as bioindicators has gained recognition over the past 20 years. Their value as indicators of atmospheric pollution is due to their large surface area and the fact that minerals and organic pollutants enter the plants mainly from the air (Carlberg, 1983). The first use of mosses and lichens as a measure of organochlorine transport was done in 1979 in a remote location in Norway (Carlberg, et al. 1983). Low levels of DDT and DDE were detected in all samples, with the parent DDT being the predominant residue. These findings were in contrast to previous biological studies. High levels of HCH

isomers were found in all samples, with the alpha isomer found in greater proportions than gamma-HCH. This may be attributed to the greater stability of alpha-HCH. Toxaphene, which has never been used in Norway, was also present but not quantified. Concentrations of individual compounds were positively correlated with relative plant distribution. The highest concentrations occurred at the most southwesterly location and the lowest concentration at the most northerly location. This suggests that the contaminant was transported by winds coming from the south and southwest pointing to Central and Western Europe as the main sources. A parallel study using fish also revealed similar insecticide residue distribution patterns, supporting the existence of long-range atmospheric transport mechanisms.

A second study of organochlorine concentrations in moss was conducted in the Norwegian Arctic in 1983 (Thomas, 1986). Lower levels of HCH isomers were detected in this study; with levels of 4.2 ppm for alpha-HCH and 1.2 ppm for gamma-HCH, compared to a mean concentration of 25 ppm for alpha-HCH and 14 ppm for gamma-HCH in the previous study. The author concluded that the HCH present could only originate from long range atmospheric transport rather than a local source. As with the findings of Carlberg (1983), the most northern and remote sites showed the lowest levels of HCH contamination, however, a statistically significant regional variance was not found.

A similar study was conducted in Iceland (Thomas and Schunke, 1984) where pasture is dominant land use and pesticides are rarely used. Levels at ppb range of HCH isomers and heptachlor epoxide were detected in all samples. In contrast to the findings of Carlberg (Carlberg, et al. 1983), the distribution of chlorinated pesticides in mosses indicated background levels at all locations with no correlation between amount and investigation site.

Further studies in 1979 and 1980 in Bavarian West Germany (Thomas, 1984) analyzed moss for organic contaminants. Concentrations of HCH isomers were at similar levels as in Norway (0.3-35.4 ppb) but, in contrast, showed higher gamma-HCH than alpha-HCH. These results possibly indicate a local pesticide source since agriculture is a major industry in Central Europe and pure lindane (gamma-HCH) is used.

Lichen samples were taken from altitudes of 1200 and 1800 m in Southern France near the Mediterranean Sea in 1986 (Villeneuve, et al. 1988). Low levels of HCH isomers, DDT, DDD, DDE and toxaphene were found; the concentrations being greatest at the highest altitude. The author speculated that these may have been transported by winds from the agricultural areas in the Rhone Valley. The results, when compared to other studies, showed similar levels to Italy, Norway and France, but higher levels than remote areas of Northern Sweden and the Antarctic. The proportion of alpha-HCH to gamma-HCH was approximately equal.

INSECTICIDE CONTAMINATION OF SURFACE WATERS

Evidence concerning the atmospheric transport of insecticides has not only included bioindicators, but also surface water and snow from remote locations. These surveys have found pesticide residues in areas as pristine as the Arctic and Antarctic. Contaminated water samples have also been found at isolated oceanic locations. The residues found in these locations support the hypothesis that the atmosphere is an important media in the global dispersion of these pesticides. Table 2 gives a summary of residue levels found in water analyses.

Organochlorine residues have been found in surface waters of many widespread continental locations, including western Canada (Gummer, 1980), Great Lakes region, (Glooschenko, et al. 1976; Stevens and Neilson, 1989; Poulton, 1987), Spain (Baluja, et al. 1985), Hawaii (Bevenue, et al. 1972), and Barvaria (Schrimpff, et al. 1979). Residues have been quantified for low levels of DDT and HCH isomers, dieldrin, chlordane, aldrin, heptachlor and heptachlor epoxide, endosulfan, and toxaphene. Residues are at very similar levels, although regions of sampling are thousands of kilometres apart. Contamination may in part reflect other sources, such as surface and ground water runoff and possibly historical use, but most authors have concluded that atmospheric transport is responsible for translocation of these residues. Their opinions are based on the remoteness of sample locations and the similarity of concentrations between widespread locations.

The analysis of surface water and snow over the past two decades in the Arctic indicates the contamination with DDT residues, HCH isomers, dieldrin, chlordane isomers, beta-endosulfan, and heptachlor. One of the earliest studies of insecticide contamination was conducted from 1979 to 1980 by the examination of snow pack and surface water samples collected from Ellesmere Island (McNeely and Gummer, 1984). Measurable concentrations of lindane and alpha-HCH, dieldrin and DDT were detected at a number of sites. Traces of alpha- and gamma-chlordane and alpha-endosulfan were also detected.

In 1981, analysis of water samples from the Hudson Bay lowlands (McCrea and Fischer, 1986) revealed alpha- and gamma-HCH, chlordane, DDE and dieldrin. Alpha-HCH was by far the most concentrated, ranging from 5-8.4 ng/L while lindane averaged 0.4-1.5 ng/L. Although the study areas were remote, concentrations of organochlorines found in water were similar to levels in industrialized Southern Ontario. Since the Hudson Bay lowland waters are free from direct contaminant inputs and all locations were at comparable levels, the probable source was the atmosphere.

Lockerbie and Claris's study (1988) of five Labrador lakes contrasts the work of McCrea and Fisher (1986). Alpha- and

gamma-HCH were identified in lake water but no other pesticides were detected. However, pp'-DDD residues were found in the lake sediments. McCrea and Wickware (1986), in a 1982 study of the Hudson Bay lowland waters reported alpha-HCH (0.5 - 12.1 ng/L), gamma-HCH (0.9 ng/L) and traces of beta-endosulfan and gamma-chlordane. No DDT group residues were detected.

Snow pack samples from Canada's Northwest Territories representing accumulation for the winter of 1985/86 (Gregor and Gummer, 1989) contained similar contaminants with HCH making up more than 75% of the total insecticides measured. Alpha-HCH (0.43-8.72 ng/L) was most abundant followed by gamma-HCH (0.2-4.08 ng/L). Alpha-endosulfan, dieldrin, cis- and trans-chlordane, heptachlor and DDE were also detected. A spatial pattern was demonstrated for alpha- and gamma-HCH. Lower results were found at coastal stations and were explained by locally induced "clean snow" diluting contaminated snow. Lower concentrations observed at Baker Lake and Ferguson River, located well inland are "indicative of reduced loadings toward the south due to fewer injections of contaminant-bearing air masses during the winter months" (Gregor and Gummer, p.565, 1989).

A study of snow samples was conducted in 1984-85 (Paasivirta, et al. 1985) at the North Pole. In contrast to earlier studies in the Arctic, no detectable organochlorine compounds could be found in any of the snow samples. This may be due, however, to very low precipitation at this location. The author suggested that the absence of organochlorine compounds may reflect the poor ability of snow to bind these residues. Results may be more comparable if annual fallout estimates were made.

Although Arctic contamination exists, pesticide levels are extremely low. DDT residues are declining and have been difficult to detect in the 1980's. This may indicate a general reduction of the atmospheric insecticide load over the Northern Hemisphere since the 1972 ban.

Two studies have shown that the Antarctic region has been contaminated with persistent organochlorine insecticides by aerial transport. Peterle collected the first snow samples in 1966 and 1967 (Peterle, 1969). The snow was estimated to have fallen in the previous two months. Three of five samples taken were positive for DDT, though only one in quantifiable amounts of 0.04 ng/L. The author studied air mass trajectories to the Antarctic continent and concluded that insertion of contaminated air was a possible explanation for the presence of DDT in this remote region.

The second study (Tanabe et al. 1983) was conducted in 1980 and 1982. Sea, lake water, ice and snow samples were collected from various depths in Syowa and Mizuho Stations in the Antarctic. Measurable quantities of DDT and HCH isomers were found at pg/L levels. Concentrations in snow and ice samples were much higher than in water samples. No difference was found between surface and deep snow samples suggesting that these

pollutants have been steadily transported to the Antarctica since the 1960's.

The background level of insecticide contaminants in open-ocean ecosystems has been examined in several locations. One of the first studies was conducted in 1972 by Jonas and Pfaender (1976). Water samples were collected at several depths from surface to 1000 m in the western North Atlantic Ocean. DDE and dieldrin (3.8 ng/L, 5.8 ng/L) were detected in all but four samples. DDT, DDD, lindane and aldrin were below detection limits. There were wide variations in concentrations from samples collected a few kilometres apart, but no discernible trend with distance from shore. Concentrations were uniform with depth to 1000 metres. Seawater samples from Blanca Bay, Argentina (Serucano and Pucci 1984), collected from several depths and distances from shore contained some organochlorines compounds. There was no uniform distribution but lindane and heptachlor concentrations appeared to correlate with the quantity of particulate matter in the sample.

Samples were collected from the Sargasso Sea in 1973 (Bidleman, 1974). Both pp'-DDT, op'-DDT, and chlordane were detected frequently in pg/L levels. The concentrations of chlorinated hydrocarbons were higher in the surface microlayer (150 um) than in subsurface water (30 cm). The author suggested that this enrichment may be due to atmospheric deposition on the ocean surface, or to an association with organic matter that is concentrated at the sea surface. Samples from Blanca Bay, Argentina, also showed enrichment at the surface microlayer. Organochlorine concentrations were found to be 18 times greater in the surface layer compared to bottom depths (5 to 12 m) (Sericano and Pucci, 1984).

In studies from 1975 to 1979 and 1980 to 1981, seawater was collected from the Western Pacific, Eastern Indian and Antarctic Oceans (Tanabe and Tatsukawa, 1980; Tanabe, et al. 1982b). Samples from all locations contained measurable amounts of DDT and HCH residues. Similar levels were found in the Antarctic and Pacific Oceans, whereas higher levels of DDT residues were observed in the Eastern Indian Ocean surface water. The variations of DDT residue levels was suggested to be a function of the amount of particulate matter in the oceans (Tanabe, 1982b). For all oceans surveyed DDT isomers were found in the following order of decreasing concentration: pp'-DDT, op'-DDT, and pp'-DDE.

The large amount of variation among different samples and locations make comparison difficult since many of these organochlorine pesticides tend to accumulate in sediment (Gerakis and Sticas, 1974 from Gummer 1980). Absolute concentrations at any specific time or location may also depend largely on water quality (i.e. amount of humic substance, particulate concentration).

INSECTICIDES IN PRECIPITATION

Rain and snow samples have been analyzed for organochlorine insecticides for over three decades at locations around the world to determine pollution levels, spatial and temporal trends, and mechanisms of transport of these chemicals. Table 3 summarizes results from several of these investigations. Low levels of DDT, HCH, dieldrin, chlordane, toxaphene, endosulfan, methoxychlor, heptachlor epoxide, aldrin and endrin have been identified in widespread locations.

Atmospheric dispersion and deposition have been investigated by correlating concentrations of insecticide residues in rain and snow with meteorological data that define air mass trajectories. Wells and Johnstone (1978) collected rainwater samples along the coast of the North Sea in Great Britain in 1975. The data indicated variations in spatial distributions of DDT, HCH and dieldrin, concentrations being lower at the most northerly station and higher in the south. This gradation was found to correlate with the distance which the air mass, believed to be the source of contamination, had travelled overland. Based on this data, a mean annual input for the area of the North Sea was estimated to be 1.43 tonnes of total DDT, 2.08 tonnes of total HCH and 0.27 tonnes of dieldrin.

Rainwater collected from remote areas of Southern France (Villeneuve and Cattini, 1986) contained chlorinated hydrocarbon residues which could be related to the suspected origin, agricultural areas in Europe.

Rainwater was collected off the coast of Bermuda in 1983 and 1984 (Knap, et al. 1988). Air mass trajectories were also studied. The lower values of HCH, chlordane and dieldrin in rain correlated with storms from the east that had passed over Bermuda prior to the collection. The higher concentrations of these trace organics generally came from storms with southwest trajectories which were clear sectors from the ocean. Technical HCH, lindane, chlordane and dieldrin were banned in Bermuda twelve years prior to the sampling date, therefore it is unlikely that these measurements were influenced by local sources. The highest occurrence of both alpha-HCH and lindane occurred when the general air mass transit was from North America to Bermuda, indicative of a North American source. Dieldrin appeared to be less direction dependent. Chlordane showed a more even distribution and did not appear to be influenced by the origin of the air mass. Mean residue values of HCH found in Bermuda precipitation were lower in comparison to HCH levels reported for precipitation in the United States. Although chlordane was not increased with North American air trajectories, measurements of chlordane in South Carolina were approximately 10 times those values presented in Bermuda (Bidleman and Christensen, 1979), suggesting a North American source of chlordane. Dieldrin appeared to have a similar distribution as chlordane, with higher

concentrations found in North America (a factor of 3-5) than in Bermuda, but lower concentrations in remote areas.

Rain samples were collected in 1984 (Strachan, 1988) in widely separated locations; Northern Saskatchewan, the Great Lakes region and on the Eastern seaboard of Canada. The pesticides found, in order of decreasing concentration, were alpha-HCH, lindane, dieldrin, methoxychlor, DDT residues, endrin and heptachlor epoxide. The same compounds occurred in rain at all of the sample locations, despite the fact that they are separated by up to 3,500 km. Their presence in atmospheric samples was concluded to be the result of atmospheric transport.

Seasonal variations in concentration levels of insecticides in rain and snow have been observed. Precipitation samples collected in the Great Lakes region of Canada (Strachan, et al. 1978) showed higher concentrations of methoxychlor in spring, and consistent detection of endosulfan only in spring and summer. Dieldrin concentrations were not affected by season. Pesticide levels in snowmelt were considerably less than in rainfall, reflecting either lower volatility during cold temperatures, or decreased use during winter. Rainwater collected in Tokyo, Japan from 1968 to 1969 (Masahiro and Takahisa, 1975) in a residential area, far from where pesticides are used, also showed that the concentration of HCH in rainwater was two to eight times higher than that in snow. Levels of HCH were correlated with the months of use; June, July, August, September and October. In contrast, rainwater samples in Bermuda (Knap, et al. 1988) showed no seasonal pattern of concentrations of HCH, chlordane or dieldrin in precipitation. The difference in these studies could reflect proximity of collection area to the source of contamination.

Measurements of HCH and DDT in precipitation over relatively long periods of time, and comparisons among studies in same locations, show that these contaminants have decreased since the general ban of use in northern countries. Rain samples analyzed in Great Britain in 1975 (Wells and Johnstone, 1978) indicated a reduction by approximately one order of magnitude for total DDT, total HCH and dieldrin compared to samples collected in the same regions in 1964 and 1965 (Tarrant and Tatton, 1968). The authors note that although differences in sample locations and techniques of analysis may have contributed to the differing results, the decline was large enough to reflect a real trend. Measurements of HCH isomers at Nova Scotia and Prince Edward Island in Canada, in 1984 (Brun, 1985) showed a substantial reduction in concentration levels in rain, compared to amounts in the same region measured between 1980 and 1984. The Great Lakes region in Canada (Chan and Perkins, 1989) also experienced a noticeable decline in HCH deposition for samples collected between 1984 and 1986.

TRANSPORT OF INSECTICIDES BOUND TO AEROSOLS

Much of the early interest in determination of pesticide concentrations in air arose from the discovery of translocation of pesticide-laden dust from origins several thousands of kilometres away. These studies became the first direct evidence that pesticides can be transported over great distances via the atmosphere, survive high altitudes and be deposited in locations remote from their application.

Cohen and Pinkerton (1966) measured levels of pesticide residues in a single dust storm in Cincinnati in 1965. Based on meteorological data, it was concluded that the dust originated from Texas, several hundred kilometres away. The dust was found to contain DDT, DDE, chlordane, heptachlor epoxide and dieldrin at ppm levels, with DDT being the predominant residue.

Gram quantities of airborne particulate matter carried by the equatorial Easterlies, the Trade Winds, across the Atlantic to Barbados were collected in 1965 by Risebrough (1968). Dust samples were collected in glycerin-coated nylon screens with an efficiency of 50% for particles larger than 1 um. The dust samples underwent mineralogical and biological analysis. Along with meteorological data, the results pointed to a continental origin of the solids, with Europe and Africa, over 4500 km to the east, as the most likely sources. During one year, the total pesticide content of the air showed no evident seasonal changes. Concentrations of DDT at ppb levels (predominant,) followed by DDE, op'-DDT, and traces of DDD and dieldrin were measured. The total pesticide concentration in air, based on particulate levels, was calculated as 7.8×10^{-14} g/m^3 or 41 ppb by weight in the dust. The pesticide concentration in air was used to calculate the volume of pesticides introduced to the equatorial Atlantic by atmospheric transport, as 600 kg/yr, comparable to the transport of pollution by major river systems. This rate of input indicated the importance of wind transport to marine environments.

In a similar study, Seba and Prospero (1971) collected Trade Wind aerosols in Barbados, West Indies, in 1968. Seba and Prospero found no obvious correlation between atmospheric dust loads and pesticide loads, suggesting that the pesticide did not become airborne at the same time as the dust but rather that the pesticide was present in the air prior to the dust event in Africa. The author suggested that the pesticides were derived from either Europe or North America and brought to the Barbados by the clockwise air flow around the Azores high pressure centre. The author also noted that because of the low collection efficiency for particles below several microns diameter and the inability to sample material in the vapor phase, the actual air concentration of pesticides may have been underestimated.

Prospero and Seba (1972) made an additional series of

pesticides and dust measurements, in 1970, during a period of maximum Saharan dust transport. The average air concentrations were 57 x 10^{-15} g/m^3 for DDT and 9 x10^{-15} g/m^3 for DDE indicating there had been no major change in concentration since the original measurements made by Risebrough in 1965. Again the higher pesticide concentration occurred at times of low dust loads, further supporting the theory that the pesticides did not originate from the point of dust origin. The authors speculated that dust could scavenge airborne pollutants from lower altitudes and carry them into the ocean. This could explain the inverse pesticide/dust load relationship.

INSECTICIDE CONTAMINATION IN THE ATMOSPHERE

One of the earliest attempts to directly determine the concentration of organochlorine residues in air was carried out in 1965 (Abbott, et al. 1966). Analysis of low volume air samples by solvent scrubbing techniques indicated the presence of trace levels of HCH isomers, dieldrin, DDT, DDE and TDE. Because of low air volume and poor collection media, residues were generally non-quantifiable.

The method of direct measurement of atmospheric insecticide residues became well documented with the development of sensitive techniques allowing the sampling of high volumes of air for both vapor and particulate phases of pesticides without substantial loss from volatilization during collection. Early air samplers collected organic pesticides by scrubbing air through solvents or by impingement techniques. Total vapor and aerosols were collected in this manner. Interest in vapor/particulate partitioning led to the use of filters, but only low volumes of air could be sampled due to substantial loss of collected pesticides in the vapor-phase and particle-bound residues with increased air volumes. The most common method of air collection used in later studies allowed for both high volume air sampling and particle collection. The apparatus consisted of a high-efficiency glass microfiber filter, followed by a number of polyurethane foam plugs, found to have a high recovery rate for these insecticides.

Table 4 summarizes results of studies of atmospheric pesticide levels from locations in continental Europe, North America, the Arctic and Antarctic and over the oceans. One of the most interesting findings is the relative similarity between levels of DDT and HCH residues measured over the oceans in widespread locations. Bidleman, et al. (1981) measured chlorinated pesticides during 1977-1978 in the North Atlantic gyre at Barbados and Newfoundland. The author noted that though Bermuda is only 1100 km from North America, airborne contaminants are readily transported to the area by the Westerlies. DDT, DDE and dieldrin, along with chlordane and HCH isomers were detected at all locations. The fact that comparable pesticide levels were measured in Newfoundland, Barbados and from trans-Atlantic cruise ships strongly indicated to the researchers that the Barbados

values were typical of the North Alantic air background levels. Concentrations of pp'-DDT measured at all locations were very similar, with an overall average of 3.0 pg/m^3. The overall average reported was lower than that of samples collected in Bermuda in 1973 (Bidleman and Olney, 1974), which had a DDT range of 11 to 90 pg/m3. Both HCH isomers were found in all samples, evidence that their presence had become widespread over the North Atlantic.

Chlorinated hydrocarbons were measured in air samples taken from the Western Pacific, Eastern Indian and Antarctic Oceans in 1980-1981 (Tanabe, et al. 1982a). All sites showed the presence of DDT compounds and HCH isomers. The presence of measurable quantities of these residues in the remote Antarctic "strongly suggest that the chlorinated hydrocarbons are surely transported to the Antarctic through the atmosphere, and the residues there contribute to the bioaccumulation in the Antarctic ecosystems" (Tanabe, et al. 1982a, p. 99). HCH isomers were also detected in air (30-170 pg/m^3) taken over the Antarctic Ocean, although at lower levels as compared with other oceans. DDT and HCH isomers measured in air in the Antarctic from 1980 to 1982 by Tanabe, et al. (1983) found mean concentrations of 20-240 pg/m^3 for total DDT and 44 to 170 pg/m^3 for total aerial HCH, levels quite similar to the earlier study in the same region. Atlas and Giam (1981) reported the presence of HCH isomers in air taken at Enewetak Atoll in the Central Pacific, showing average concentrations of total HCH as 270 pg/m3. The concentration of total HCH measured near Enewetak by Tanabe, et al. (1983) at 370-450 pg/m^3 were fairly close to Atlas and Giam's reported HCH levels. Similar concentration levels in air were found in the Central Pacific of 190-320 pg/m^3, and Antarctic Ocean (110-230 pg/m^3). Bideleman and Olney (1974) reported 20-90 pg/m^3 of total DDT in air over the North Atlantic. Bidleman and Leonard (1982) also reported the presence of pp'-DDT and op'-DDT in air taken from Arabian Sea (5-126 pg/m^3), similar to earlier work by Tanabe and Tatsukawa (1980) in the mid-latitude North Pacific from Tokyo to Los Angeles, finding total DDT in air with a range of <10-120 pg/m^3.

Sources of atmospheric contamination have been proposed using correlations with meteorological data and concentration levels. Bidleman and Olney (1975) attempted to determine the potential for atmospheric transport of toxaphene, a complex mixture of polychlorinated camphenes, over the Sargasso Sea and south shore of the Bermuda coast in 1973-74. The sampling apparatus allowed for collection to be controlled by wind direction, which enabled sampling of air crossing either the open-ocean or Bermuda. Atmospheric concentrations over the Western North Atlantic ranged from <0.02 to 3.3 ng/m^3. Based on the wind trajectories and local historical use of pesticides, it was concluded that the Bermuda values were unlikely to be the result of local contamination. The mean levels of toxaphene in the Western North Atlantic were about 10 times higher than those of other pesticides presently reported in the marine atmosphere.

This is likely a result of large scale use of toxaphene and its relatively high volatility. The source is considered to be the cotton growing areas of the Southern United States. High levels of toxaphene have also been identified in North Atlantic air off the coast of Newfoundland, ranging from 57-160 pg/m^3 in 1977 to 1978 (Bidleman, et al. 1981).

Oehme and Manoe (1984) measured organochlorine levels in air over a period of two years in the Norwegian Arctic. Concentrations were correlated with air mass trajectories. The lowest concentrations of pesticides were associated with westerly winds from the Atlantic and the highest with winds from mid-England. Seasonal variation in concentrations were also observed. The concentrations of alpha-HCH were consistently lower in winter than in summer. Lower temperature and a snow-covered ground were considered reasonable explanations for decreased concentrations in the winter season. The opposite was observed for gamma-HCH where higher concentrations occurred in winter. Accelerated transformation of both deposited and atmospheric gamma-HCH to the alpha isomer in the summer season and the predominant use of purified lindane in spring were considered the cause for differing behavior of gamma-HCH. Similar observations for seasonal behavior of the HCH isomers was noted in air samples from the Antarctic (Tanabe, et al. 1983) where high concentrations of alpha-HCH were generally obtained during the austral summer (Tanabe, et al. 1983). Oehme and Stray (1982) also reported the seasonal variation of HCH isomers in the Arctic. Lower levels of HCH isomers were measured in winter, due to seasonal variation in use, or re-emission of earlier transported and deposited HCH from the ground.

THE DDT "SOUTHWARD TILT"

Global levels of DDT residues in marine air have been found to reflect current and historical use. Since the late 1960's, the use of DDT decreased substantially in the Northern Hemisphere, until it was completely banned in 1972. However, underdeveloped and tropical countries in the Southern Hemisphere are presently heavy users of DDT for malaria control and agriculture. The decrease in the use of DDT in the Northern Hemisphere and the continued use in the Southern Hemisphere, or "the southern tilt", has caused the occurrence of DDT residues in air, water and precipitation to shift predominantly to the Southern Hemisphere (Goldberg, 1975).

Air and surface water samples were collected in the North Pacific and Indian Oceans, including the Bering Sea, East China Sea, South China Sea, Bay of Bengal and the Arabian Sea in 1975-79 (Tanabe and Tatsukawa, 1980). High concentrations of total-DDT were discovered in a number of air samples off the western coasts of India and Central America, and off the southern

and eastern coasts of Asia, when compared to levels occurring in air over the Bering Sea and the North Pacific Ocean. The author concluded that the lower levels found in the North Pacific were a result of long range transport from the Asian continent and Japan by westerly winds. Levels of DDT residues showed increasing concentrations southward from 30°N latitude, correlating with an increased use southward in Asia. In contrast to the higher concentrations and large variabilities found in samples from widespread locations in the Southern Hemisphere, samples from the Northern Hemisphere exhibited the presence of DDT at low concentrations (Bidleman and Olney, 1974). Although locations in the Northern Hemisphere were thousands of kilometres apart, DDT concentrations were very similar. This may be indicative of long range transport over the globe.

Similar evidence that areas consuming DDT have shifted from northward to southward was indicated by measurement of residue levels in the North Atlantic (Barbados and Newfoundland) compared with the Northern Indian Ocean (Bidleman and Leonard, 1982). Air samples from Southern Hemisphere had an average 25-40 times the 3.0 pg/m^3 North Atlantic level of DDT (Bidleman, et al. 1981). In the equatorial and Northern Arabian Sea, Persian Gulf and the Red Sea, the oceans are surrounded by countries which are among the heaviest users of DDT in the world. Nearer land in the Arabian Sea, there was also an observable trend toward higher DDT levels with highly variable results, compared to the uniform DDT levels found in the North Atlantic samples collected thousands of kilometres apart. Average total DDT concentration of 75 pg/m^3 over the Arabian Sea measured in 1976 to 1977 were lower than a mean of 440 pg/m^3 from 1976 (Tanabe and Tatsukawa, 1980).

Tanabe, et al. (1982) also observed a definite increase in DDT residues on the Asian continent in 1980-1981. However, the differences in total DDT levels between the Northern and Southern Hemispheres were found to be smaller than previously observed (Tanabe, et al. 1982). The heavy use of DDT in recent years in tropical regions of Mexico and Central America is reflected in increased levels of DDT residues in marine air over the Gulf of Mexico (Giam, et al. 1979) and off the western coast of Central America (Tanabe and Tatsukawa, 1980).

Atmospheric levels of DDT were found to decline when measured southward from Asia to the Antarctic (Tanabe and Tatsukawa, 1983) suggesting that the lower latitudes serve as a major source of DDT for transport to the Antarctic. Furthermore, the author also noted that the relative isomer composition found in the Antarctic air samples closely resembled formulation compositions used in the tropics (pp'-DDT > op'-DDT > DDE).

DDT "AGE"

The presence of DDT in the Northern Hemisphere many years after its last use has led to speculation as to the source of contamination. Evidence has shown that recent levels of contamination are indications of "new" sources of DDT being transported from areas of current use, rather than redeposition of DDT used in the past.

The levels of total DDT measured in rain water and snow melt samples taken from the Great Lakes region in 1976 and 1977 were constant over the study period (Strachan, et al. 1978) suggesting input from sources removed from the Northern Hemisphere. Strachan also found that the predominant isomer present was pp'-DDT (76%) rather than the principle metabolite DDE, indicating fresh usage. Similar observations were made from air and water samples in College Station, Texas, in 1979-1980 (Atlas and Giam, 1988) where a DDE:DDT ratio of 0.87 was observed, further indicating a new input of DDT into North America. By comparison, regions still actively using DDT demonstrate high ratios of DDT:DDE, similar to the isomer composition of the formulation, which is approximately 70-80% pp'-DDT and 15-20% op'-DDT (Tanabe et al., 1980).

Rappaport, et al. (1985) measured the surfaces and cores from peat bogs in Eastern North America in 1981-1983. These bogs have been found to be an ideal indicator of atmospheric deposition, since they receive all pollutant inputs from the atmosphere, and hydrophobic organics are largely preserved in the historical profile. Rates of DDT accumulation were determined in the peat cores. Profiles of total DDT accumulation were found to be comparable with the known historical use. The maximum concentration occurred about 1960 with a dramatic decline following the 1972 ban. However, two observations pointed to a "new" input of DDT to these bogs. First, the core samples illustrated the rapid environmental response to the DDT ban, then an increase in accumulation rate was observed in the last five years. That is, the rates of accumulation diminished more slowly than those immediately after the ban. Second, the small amount of transformed DDT, as DDE and DDD, in surface peat (21%) and precipitation (23%) suggested that current inputs do not represent recycled resides. The composition of total DDT at the surface of these cores closely resembled the mostly untransformed DDT deposited prior to the ban. The author concluded that the fresh source of DDT inputs to North America is a result of use in Central America and Mexico. Estimated inputs of fresh DDT from these sources were calculated as 0.2 to 1.1 ug/m^2/yr, higher than inputs to the mildly contaminated North Atlantic, and lower than the likely source of Mexico and Central America.

THE "NORTHWARD TILT" OF HCH

High HCH levels have been found in the Northern Hemisphere, especially along the Asian continent (Tanabe, et al. 1982). Levels of 1100-2000 pg/m^3 in air, 3100-7100 pg/L in surface water reflect the high use of HCH type pesticides. Earlier work by Tanabe and Tatsukawa (1980) found relatively uniform distributions of atmospheric HCH isomers in the North Pacific and Indian Oceans, except off the coast of India and Japan, where fairly high concentrations were found. HCH isomers were also detected in air over the North Atlantic and in the Indian Ocean (Bidleman, et al. 1981). HCH concentrations in air increased northward from 40° N in Asia, while DDT levels increased from 30° N southward. High HCH levels were also reported in air around the Asian continent (Bidleman and Leonard, 1982), with mean levels of 590 pg/m^3 in the North Pacific, 3200 pg/m^3 in the Arabian Sea and 590 pg/m^3 in the Bay of Bengal.

Measurements of airborne HCH residues were also found to decrease towards the Antarctic (Tanabe, et al. 1983), and as expected, mean levels of 0.09-0.17 ng/m^3 in air in the Antarctic were found to be substantially lower compared to measurements of air over the Pacific and Indian Oceans (Tanabe, et al. 1982).

ISOMER COMPOSITION OF HCH

As mentioned above, two pesticide formulations of HCH are commercially available; technical HCH and lindane. Technical HCH consists of approximately 70% alpha-HCH and 13% gamma-HCH while lindane is a formulation of purified gamma-HCH isomer. Lindane has generally replaced technical HCH over the past few years as the predominant type used. This shift to lindane use is reflected in the isomeric composition found in atmospheric samples.

Tropical and southern countries may, however, still be using both formulations of HCH. Samples from Asia, the North Atlantic, the North Pacific and the Antarctic all exhibit a greater alpha- than gamma-HCH concentration (Bidleman and Leonard, 1982; Bidleman, et al. 1981; Tanabe and Tatsukawa, 1980; 1983). However, Tanabe, et al. (1982) measured HCH in air and, while also finding higher alpha- to gamma-HCH ratio in the northern oceans studies, the relative concentration was reversed in the tropical regions in both air and water. It was speculated that this trend is the result of increased use of lindane in these regions.

The alpha- to gamma-HCH ratio has proved to be a useful tool in determining the "age" of HCH residues in remote environments. The alpha- to gamma-HCH ratio also aids in source differentiation. This is based on evidence that gamma-HCH can be transformed to the alpha isomer by UV-radiation (Oehme and Manoe, 1984). Therefore, an "old" air mass contaminated with HCH will contain a higher alpha:gamma ratio relative to a "new"

source of atmospheric HCH.

Air samples collected in the Norwegian Arctic gave an alpha:gamma ratio greater than 100:1 in August, 1982 (Pacyna and Oehme, 1988). This can be compared to alpha:gamma ratios found in the Great Lakes region of 2:1 in 1986 (Chan and Perkins, 1989), a ratio of 0.16:1 found in rainwater in the Mediterranean (Villeneuve and Cattinni, 1986), Bavarian rainwater samples of 1-2:1 (Schrimpff, et al. 1979), and 0.74-1.01:1 in rainwater in Japan. These low ratios indicate a relatively new source of HCH. In contrast, samples from other remote locations have shown relatively high alpha:gamma ratios; 15:1 in the Arctic (Oehme and Manoe, 1984), 4-9:1 (Knap, et al. 1988), 17:1 in the North Atlantic (Atlas and Giam, 1981), 6-8:1 off the coast of the Canadian Maritimes (Brun, 1985) and 8.3:1 found in Texas in 1979 - 1980 (Atlas and Giam, 1988). Increases in alpha:gamma ratios have also been found over a two year sample period in rainwater collected in Atlantic Canada, suggesting "aging" of the source (Brun, 1985).

The relative concentrations of alpha- to gamma-HCH have been found to be highly dependent on seasonal conditions. Isomer composition measured in air samples in the Arctic exhibited a lower alpha:gamma ratio in winter/spring (10:1) than in the summer/fall (50:1) season. This may indicate either isomerization may be more efficient in the summer/fall season or the use of purified lindane in the spring (Oehme and Manoe, 1984). The author also speculates that the differing seasonal behaviors of the HCH isomers may indicate re-emission of previously transported and deposited alpha HCH from the ground when temperatures rise in the spring.

The same study (Oehme and Manoe, 1984) also found two distinct maxima in both concentration and relative composition of HCH isomers. The authors proposed that there are likely two different sources contributing to Arctic contamination. Comparison of these relative compositions with air mass trajectories indicated long range transport from Europe/Soviet Union as one source, and United States/Asia, as the second source.

Alpha- and beta-HCH ratios were examined together with air masses trajectories in Bermuda (Knap, et al. 1988). The results did not clearly point to a source since ratios were higher in air masses from North America and lower in "cleaner" ocean air masses. The opposite would be expected since ocean air should contain pesticide residues from an older source considering the distance of transport compared to a newer North American source. The ratios only provided evidence that the sources of HCH contamination in the atmosphere were not relatively new.

PHYSICAL FORM OF INSECTICIDES IN THE ATMOSPHERE

Airborne organic contaminants can exist in several physical states. These include the gaseous or vapor phase, liquid aerosols, or solid particles consisting of either the pesticide in a pure state or adsorbed on surfaces of other airborne particles. The physical state of the contaminant determines the residence time of an organic pollutant in the atmosphere.

Many of the early measurements of pesticide residues in the atmosphere were made with air pollution sampling devices designed to collect total suspended particulate matter (Cohen and Pinkerton, 1966 Abbott, et al. 1966). This lead to a hypothesis that pesticides existed predominantly adsorbed onto airborne particulates. Present knowledge suggests that atmospheric organic pollutants exist predominantly in the gaseous state, with a smaller proportion adsorbing to airborne particulates.

Samples for measurement of pesticide residues in the atmosphere over the Sargasso Sea (Bidleman and Olney, 1974) were collected using glass-fiber filters and polyurethane foam. The filter was capable of retaining particles greater than 0.015 um. This allowed sampling of both vapor phase and particulate-bound pesticides in the atmosphere. Most of the DDT and chlordane were trapped on the polyurethane foam, with less than 5% associated with the filter. Although the possibility of volatilization from the filter existed, these finding suggested that earlier atmospheric measurements of residues by particle entrapment had greatly underestimated levels of airborne contamination. The conclusion that DDT likely existed mostly in the vapor phase was substantiated by the fact that concentrations of DDT in Bermuda air were one to two orders of magnitude greater than the earlier results determined by particle collection in nylon screens. Other researchers have also found a similar increase airborne pesticide levels when compared to the dust collection studies in ocean air (Bidleman, et al. 1981).

Several studies have provided further evidence of the predominance of chlorinated hydrocarbons in the gaseous phase in the atmosphere. DDT, dieldrin and chlordane concentrations were found to be <10% filter-retained (Bidleman, et al. 1981). Toxaphene was found to be less than 5% of the total level in air retained by the filter (Bidleman and Olney, 1975). Generally, less than 10% filter retention has been found for the insecticides toxaphene, HCH isomers, chlordane and dieldrin (Chevreuil, et al. 1989; Bidleman, et al. 1976; Giam, et al. 1980; Oehme and Manoe, 1984; Bidleman, et al. 1981; Atlas and Giam, 1988; Wittlinger and Ballschmiter, 1987; Bidleman and Leonard, 1982; Knap, et al. 1986; Bidleman and Christensen, 1979). DDT appears to have a slightly higher potential for binding to particulates in air. Filter-retained DDT residues have been shown as 70% (as DDE) (Chevreuil, et al. 1989), 17% DDT (Bidleman and Christensen, 1979) and <5% for DDT (Wittlinger and

Ballschmiter, 1987) depending on sampling location.

Vapor-aerosol partitioning in the atmosphere depends on the vapor pressure, size, surface area and organic content of the suspended particles (Eisenreich, et al. 1981). Atlas and Giam (1988) discovered seasonal variation affecting the amount of particulate-bound DDT residue. Greater proportions of filter-retained DDT and DDE were observed in winter (DDT = 5.5%, DDE = 0.9%) than in summer (DDT = 1.4%, DDE = 0.3%), likely due to the temperature effect of the partition coefficient. Variations in the particle-associated percentage of DDT residue were also found to be dependent on the area of collection. Filter-retained percentages of pp'-DDT averaged 4% for the open ocean environment of the Arabian Sea. However, 15% filter-retention of DDT was discovered over the Persian Gulf, Red Sea and coastal Arabian sea (Bidleman and Leonard, 1982). Higher proportions of particulate-bound DDT seemed to be associated with proximity to land. It is assumed to be a result of higher airborne particulate densities closer to the coast than in the open-ocean environment. The available aerosol surface area would be a limiting factor for the total mass of organic compounds found as particle-bound. Higher particulate density was also observed to affect DDT partitioning in rain collected in Britain. Reduction in DDT levels were found on the glass-fiber filters corresponding to reduced total airborne particulate density (Wells and Johnstone, 1978).

PROCESSES OF REMOVAL

Pesticides in gaseous and particulate phases may be removed from the atmosphere by precipitation scavenging or by dry deposition by sedimentation and impaction of particles. The relative importance of these mechanisms to efficiently remove pesticide contaminants from the atmosphere has been examined.

The relative importance of these processes depends on the distribution of the organic matter between vapor and aerosol, particle-size distribution, and Henry's law constant. Based on theoretical considerations and general chemical properties, Junge (1975) considered that wet-removal rates for organic vapors are generally low. Unless the vapor pressures of the compounds are extremely low, most of the material will be present in the gaseous phase so that residence time will be fairly long (greater than one year) and the constituent can spread throughout the troposphere. Attachment of trace gases to atmospheric aerosols and subsequent removal by washout and rainout were considered a much more efficient mechanism of removal, with an implied global residence time of 50 to 100 days for these organic residues.

The relative efficiency of wet deposition as a removal mechanism has been examined by comparing concentrations of pesticides in air and in rain and calculating partition coefficients between water and air, expressed as washout ratios.

Measurements of air and rain in several widespread locations have shown close agreement to washout ratios calculated from theoretical considerations. Table 5 summarizes these results, along with estimates of atmospheric residence times.

Studies by Atkins and Eggleton (1971) supported Junge's suggestions that removal of pesticide vapors by rainfall is relatively inefficient and indicated that particle scavenging is the primary removal mechanism for wet deposition of pesticides. Based on the findings that these pesticides occur in the atmosphere primarily in the vapor state, washout ratios for the pesticides lindane, dieldrin and DDT were calculated using partition coefficients for gases between air and water. Ratios were determined to be 14 for lindane, 2.3 for pp'-DDT, and 0.65 for dieldrin. Comparisons to observed washout ratios at Cornwall House in London in 1965 (Abbott, et al. 1966) were found in close agreement for lindane (6-13), lower than that observed for dieldrin (2.4) and much lower for DDT (65). Therefore, the authors concluded that lindane was present in the London atmosphere in the gaseous state, dieldrin was almost entirely in the gaseous phase, and a substantial proportion of DDT was in the particulate form. This conclusion agrees with findings that the larger proportions of DDT were trapped on glass-fiber filters compared with HCH in studies discussed earlier. Rates of deposition of radio-labelled pesticides were measured in a wind tunnel and estimates of removal rates were calculated for both washout and dry deposition. The values obtained for all three pesticides showed dry deposition as the most effective removal process. Estimated residence times were calculated as lindane at 17 weeks, pp'-DDT at 26 weeks and dieldrin at 28 weeks.

Filtered rainwater and dry deposition were collected in France (Villeneuve and Cattini, 1986). Fluxes of pp'-DDT, DDE, toxaphene and HCH isomers were calculated for wet and dry deposition. Dry deposition fluxes were at least one order of magnitude higher than those induced by the wet deposition process for input into the Mediterranean sea. These results are similar to Atkins and Eggletons' observations (1971).

Atlas and Giam (1988) measured air and rain samples along with dry deposition at College Station in Texas in 1979 to 1980. Dry deposition results were found to account for 7 to 22% of the total concentration measured in an average rain in 24 hours and, therefore, considered relatively minor in contribution. They found an inverse correlation between rainfall volume and concentration in rainfall with a 2/3 power relationship for dieldrin, chlordane, DDT and toxaphene. However, others have noted independence of concentrations with volume of rainfall (Wells and Johnstone, 1978). This behavior has been found to be characteristic of rainfall scavenging of particulate matter, suggesting that particle scavenging is an important mechanism for wet deposition compared to wet removal of gaseous species. This observation agrees well with both Junge's (1975) speculations based on theoretical premises, and Atkins and Eggleton (1971)

results in the laboratory. This relationship was not observed for the more water soluble HCH isomers, which may have more important processes of gaseous phase equilibration with raindrops. In contrast to this speculation was the observation that filtered rain samples from Tokyo had a large proportion of HCH associated with particles of less than 0.45 um in size (Masahiro and Takahisa 1975). Significant correlations for pesticide concentration in rain were observed for alpha-HCH:gamma-HCH, between alpha-HCH and dieldrin, and between DDE and chlordane, suggesting different removal processes for each group.

Removal of chlorinated insecticides from the atmosphere was investigated further by Bidleman and Christensen (1979) in South Carolina. Dry deposition velocities were measured for chlordane (0.068 cm/s) and pp'-DDT (1.3 cm/s). Higher velocity correlated with lower volatility (DDT) and vice versa (chlordane), which exhibits a greater attachment of DDT to aerosols. Washout ratios were measured as 66:1 for pp'-DDT, 2.2:1 for chlordane and 22.2:1 for toxaphene. Washout ratios were higher for DDT than those calculated by the equilibrium coefficient of only 0.3 between air and water, suggesting washout of particles rather than vapor dissolution in rain. A calculated toxaphene washout ratio of 90 compared to an observed ratio of 246 indicates the potential for incorporation into droplets at rain-forming heights. Also noted was a smaller difference between wet and dry removal rates for DDT than earlier noted.

Samples of sediment collected from the Sargasso Sea off the coast of Bermuda show a significant correlation between chlordane and dieldrin, between alpha- and gamma-HCH, and between chlordane and dieldrin in rain samples in the same location (Knap, et al. 1988). The total deposition of chemical was compared with the size of the storm responsible. Variation of volume of rain with concentration of the pesticides was plotted, showing a poor correlation for alpha- and gamma-HCH and dieldrin. Chlordane was far more evenly distributed. This pattern was also found when correlated with air mass from North American sources. Dieldrin was less direction dependent than HCH, and chlordane was completely unaffected by origin of air mass. A stronger single storm bias and direction dependence would be expected if washout of particles were responsible for these compounds in the Bermuda region. Similar observations were noted by Bidleman and Christensen (1979) for chlordane, which was found to be removed more slowly by rainfall and dry deposition than was DDT. Therefore, chlordane should have a longer atmospheric lifetime and hence, more homogenous distribution. It follows that wet deposition by particle scavenging is expected to be less important in remote open ocean regions containing few anthropogenic particles than in continental air.

Surface water and air samples collected from the Sargasso Sea gave estimated lifetimes of 51 days for DDT (Bidleman and Olney, 1974). This is much shorter than the proposed atmospheric

residence time for DDT of 3.3 years, based on DDT production figures and assuming rainfall is the dominant method of removal from the atmosphere (Woodwell, 1971).

CONCLUSION

Considerable quantities of chlorinated hydrocarbons have become globally distributed, primarily by the atmospheric route. No location has been left untouched by these persistent xenobiotics. Insecticides such as DDT and HCH continue to be transported to remote environments because of the extensive and uncontrolled use in tropical and developing countries. Little is known of the physical or chemical forms of these residues in air, and many questions still remain unanswered regarding their lifetime in the troposphere before their removal by rainfall, photochemical degradation or other processes. In addition, little is known of the degradation at high atmospheric levels. Highly toxic alteration products may exist undetected in the atmosphere.

Although levels of insecticides residues currently detected in air, water, precipitation and biota are generally so low as to be considered of little consequence to health, the effect of this chronic addition to the total body burden is unknown. Further investigation is necessary to fully understand the contribution of the atmospheric transport of pesticides to global pollution.

Table 1: Insecticide Levels in Biota (ppb)

Location	Year	Species	Ref	ppDDT	opDDT	DDE	DDD	TDE	t-DDT	a-HCH	g-HCH	b-HCH	t-HCH	Dieldrin	Aldrin	Heptachlor	Chlordane	Toxaphene
Antartica	64	penguin	53	0-69		7-83	0-16		13-152									
		seal																
Antartica	67	penguin	63	1-12		1-48		ND-6		0-5	0-5	ND-8		1-10		ND-6		
		fish		6-20		2-13		0-18		1-7	1-4	2-8		1-9		2-4		
		squa		230-2500		890-26000		ND		ND-4	ND-6	ND-4		ND		35-730		
		shag		3-23		11-140		ND-18		ND-2	ND-3	3-10		2-6		ND-2		
Baltic Sea	65	fish	21	600-14000					6000-31000									
		seal		17000-62000					96000-13E4									
		birds		ND-20000					57E4-25E6									
Baltic/North Sea	74	fish	29						6800-8000								500-600	900-13000
		guillemot							170000								700	17000
		seal							970000								10000	11000
North Sea	74	crab	34			8-146				4-40	6-64							
											ND-16							ND-350
Mediterranean	83	zooplankton	15	ND		ND-28	ND-14											
Arctic (Greenland)	72	seal, bear	19	ND	ND	150-1250								ND	28-3060	ND-39		
		fox, sheep																
Arctic (Cdn)	81	fish	37		ND	ND-4				ND-3	ND			ND	ND	ND	ND	
Labrador	80	fish	35	ND	ND-31	ND-840				ND-3	ND-33							
California (US)	78	sheep	68	ND-30		ND-80	ND-40					ND-70		ND-90	ND	ND-60		
														1-7	ND-11	ND-3		
Maine (US)	81	fish	28			11-34	ND-7			ND-19								
Norway	79	moss	16	0.4-20		0.1-5				6-100	3-65							
										(25)	(14)					0.1-1.4		
Barvaria	79	moss	66							0.3-30.7	2.3-35.4							
France 1200 m	86	lichen	70	8.7	4.7	2.5	0.7			28	24							130
1500 m				12.2	4	13.3	1.4			126	130							190

Table 2: Insecticide Levels in Surface Water (ng/L)

Location	Year	Ref	ppDDT	opDDT	DDE	TDE	t-DDT	a-HCH	g-HCH	b-HCH	t-HCH	Dieldrin	Chlordane	Aldrin	Heptachlor	Endosulfan	Toxaphene
Hawaii	71-72	6	5-5								3-5	1-2					
Western Cdn	71-77	27	ND		ND			ND-20	ND-86			ND		ND-2	ND-7	ND-11	
Hamilton Harbour	82	45	ND	ND	ND	ND		ND-6	ND-59	ND			ND-4		ND-1	ND-4	
Great Lakes	86	54	ND	ND	ND-0.139	ND		1.1-10.9	0.3-2.5			0.075-1.11	0.018-0.102	ND	0.026-0.306	ND	
Bavaria (snow)	78	50						4	6			6		4			
Donana, Spain	81-83	5					210				30						
REMOTE SITES																	
Ellesmere Island	79-81	38	ND-2	ND-4								ND-4	ND-2			ND-2	
Hudson Bay	81	37	ND	ND	0.1	ND		5-8.4	0.4-1.5			0.1-0.4	0.1-0.5	ND	ND	ND	
Moose River, Cdn	82	38	ND	ND	ND	ND		0.5-12.1	ND-1.6			ND	ND-1.0	ND	ND	ND-0.6	
NWT (snow)	85-86	26	ND	ND	ND-0.07	ND		0.8-8.7	0.2-5.3			0.11-1.63	ND-0.48		ND-0.41	0.09-1.34	
MARINE											0.2-2.3						
Antarctic Ocean	82	61					0.001-0.02					ND					
Sargasso Sea	73	7	ND-2.1	ND-0.3								ND		3.8			
North Atlantic	72	59	ND		3.8						0.17-22.6						
North Pacific	75-79	59					0.001-1.35										
Indian	80-81	59	0.003-0.011	0.001-0.032	0.001-0.011		0.005-0.125	0.021-3.4	0.11-3.7	0.005-1.0	0.29-7.3						
Bianco Bay	80-81	52					ND-602	2.5-219.6	5.3-320.4			ND		ND-853	ND-389		ND-30
Mediterranean	82	15					(67)	(48.2)	(54.2)								

Table 3: Insecticide Levels in Precipitation (ng/L)

Location	Year	Ref	DDT	DDE	TDE	DDD	t-DDT	a-HCH	g-HCH	b-HCH	t-HCH	Dieldrin	Chlordane	Endosulfan	Methoxychlor	Toxaphene
England	64-65	72	1-4									3-36				
London England	65	1	ND-400	ND-70	ND-100			10-40	20-155	ND-90		15-95				
British Isles	66-67	62	18-66	7-28	5-34				32-121	5-35		2-16				
British Isles	75	71					0.3-44				5.7-17	0.2-1.4				
Ohio, US	65	20	20-130	ND-50					6-50				0.017-0.38			0.33-7.6
South Carolina (ng/kg)	73-77	10	ND-6.8									0.3-6	0.3-2.7			10-26
Texas	79	4	0.3-6	0.3-2.7				2.8-34.6	0.3-0.78			1-97	ND-3			
Hawaii	71-72	6	1-14								ND-9	1-2		ND-5	2-8	
Great Lakes	76-77	55					2.5	20	7			0.56			2.4	
Great Lakes	83	56	0.11	0.12		0.11		17.4	5.9							
North East US	83	47	0.1-0.55				0.1-1.36					ND	TR	TR		
Atlantic Canada	84	14					ND	ND-15	ND-2			ND			ND-1.7	
Canada	84	57	0.11-0.23	ND-0.13		ND-0.14		6.2-17	1.2-6.7			ND				
Great Lakes	86	17	ND-1.8	ND-2.5	ND-1.2			0.4-35.7	0.5-23			ND-5.9	ND-1.2	ND-14		
Tokyo	69	33						13-830	11-398							
Arabian Sea	78-78	12	0.6					7.7	1.9							
Bermuda	83-84	33						0.005-6.0	0.09-0.94			0.008-0.913	ND-0.466			
France	86-87	16						ND-16	11-90							ND-53
Mediterranean	86	69	0.25-5.1	ND-0.15		ND-1.2		1.5-8	11.1-75.5							

Table 4: Insecticide Levels in the Atmosphere (pg/m3)

Location	Year	Ref	ppDDT	opDDT	DDE	TDE	t-DDT	a-HCH	g-HCH	t-HCH	Dieldrin	Chlordane	Toxaphene	Endosulfan	Heptachlor
London	85	2	3		4-7	3		1	5-11		18-21				
Texas	79-80	4	10-160		40-860			80-2300	10-1600		20-230	320-2640	1000-2500		
Paris	86-87	18			<50-220			<10-840	100-3400						
West Germany	86	73	1-43		4-39			110-1300	180-11000						
Sargasso Sea	73	7	10-90	9-37								ND-170			
Bermuda	73-74	8											<20-3300		
North Atlantic	77-78	12	1-14		<0.3-6.4						1.1-24	3.9-64		5.2-38	
Gulf of Mexico	77	23	10-78		10-180										
North Pacific	75-79	58					<10-10900								
North Indian Oc	76-78	12	4.7-580	<3-520							<1-35	<3-35		1.7-120	
Western Pacific	80-81	60					190-320			370-450					
Antarctic Ocean	80-82	61					110-230	161-1290	12-50	90-170					
Arctic Norway	80	40					20-240			44-170					ND-4
Arctic Norway	80-81	41					ND	161-1290	12-50						
Arctic Norway	82-84	43	N)	ND	ND			38-1550	0.1-102			0.5-5.4			
Baltic Sea	88	48						20-900	20-2000						

Table 5: Washout Ratios (C rain/ C air) and Estimated Residence Time of Insecticides

Reference	Description	ppDDT	ppDDE	g-HCH	a-HCH	Dieldrin	Chlordane	Toxaphene
Junge, 1975	calculated residence time			organochlorines	50 b 100 days			
Atkins & Eggleton, 1971	calculated (gaseous)	2.3		14		0.65		
	from Abbott, 1965	65		6-13		2.4		
	residence time	26 wks		17 wks		26 wks		
Bidleman, 1974 Sargasso Sea	residence time	51 days						
Bidleman & Leonard, 1982	Arabian Sea	68			23-41			
Bidleman et al, 1981				organochlorines	41-67 days			
Atlas, Giam,	College Station, Texas	35, 69	3.8	37, 14	26, 17	8.9	1.9, 2.2	12.3, 22.2
Bidleman and	calculated (gaseous)	0.3						90
Christensen, 1979	South Carolina	87					8.4	246
Wittinger & Ballschmiter, 1987	West Germany			10.3				
Bidleman et al, 1978	residence time	60-90 days						

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